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(54) **Compositions of antistatic styrenic polymers.**

(57) The invention relates to a composition comprising, for 100 parts by weight, 99-60 parts of a styrenic polymer (A), 1-40 parts of (B)+(C), (B) being a polyamide block and polyether block copolymer essentially comprising ethylene oxide units (C₂H₄-O)—, (C) being a compatibilizer of styrene selected from among block copolymer comprising at least one polymerized block comprising styrene and at least one polymerized block comprising methyl methacrylate, (B) 1 and (C) ranging from 2 to 10.

Compositions of Antistatic Styrenic Polymers

The invention relates to compositions of antistatic styrenic polymers and more precisely a composition comprising a styrenic polymer (A), a copolymer (B) of polyamide blocks and polyether blocks comprising essentially ethylene oxide units —(C₂H₄—O)— and a compatibilizer (C).

The object of the invention is to give the styrenic polymer (A) antistatic properties. The formation and retention of static-electricity charges on the surface of most plastics are known. The presence of static electricity on thermoplastic films results, for example, in these films sticking to one another, making them difficult to separate. The presence of static electricity on packaging films may cause the accumulation of dust on the articles to be packaged and thus impede their use. Styrenic resins, such as polystyrene or ABS, are used to make cases for computers, telephones, televisions, photocopiers, and numerous other articles. Static electricity causes accumulation of dust, but most importantly can also cause damage to microprocessors or components of electronic circuits present in these articles. For these applications, it is generally desirable to find compositions based on styrenic resin whose surface resistivity measured according to standard IEC93 is less than $5 \cdot 10^{13}$ O/□ or whose volume resistivity measured according to standard IEC93 is less than $5 \cdot 10^{16}$ O/cm (the type of resistivity being chosen as a function of the application, given that these two types of resistivity always increase in the same direction). This is based on the consideration that these resistivities provide adequate antistatic properties for certain applications in the field of polymer materials in contact with electronic components.

The prior art has described antistatic agents, such as ionic surfactants of the ethoxylated amine or sulfonate types which are added into polymers. However, the antistatic properties of the polymers depend on ambient humidity and are not permanent, since these agents migrate to the surface of the polymers and disappear. Copolymers containing hydrophilic polyether blocks and polyamide blocks have therefore been proposed as antistatic agents, these agents having the advantage of not migrating and

therefore of providing antistatic properties which are permanent and also independent of ambient humidity.

The Japanese patent application JP 60 170 646 A, published September 4, 1985, describes compositions consisting of 0.01 to 50 parts of polyether block amide and 100 parts of polystyrene, these being used to make sliding parts and wear-resistant parts. The antistatic properties are not mentioned.

Patent application EP 167 824, published January 15, 1986, describes compositions similar to the preceding compositions, and according to one embodiment of the invention the polystyrene may be blended with a polystyrene functionalized by an unsaturated carboxylic anhydride. These compositions are used to make injection-molded parts. The antistatic properties are not mentioned.

The Japanese patent application JP 60 023 435 A, published February 6, 1985, describes antistatic compositions comprising from 5 to 80% of polyetheresteramides and from 95 to 20% of a thermoplastic resin chosen from polystyrene, ABS and PMMA among others, this resin being functionalized by acrylic acid or maleic anhydride. The amount of polyetheresteramide in the examples is 30% by weight of the compositions.

The patent EP 242 158 describes antistatic compositions comprising from 1 to 40% of polyetheresteramide and from 99 to 60% of a thermoplastic resin chosen from styrenic resins, PPO and polycarbonate. According to a preferred embodiment, the compositions also comprise a vinyl polymer functionalized by a carboxylic acid that can be for example a polystyrene modified by methacrylic acid.

The international patent application PCT/FR00/02140 indicates the use of copolymers of styrene and of an unsaturated carboxylic acid anhydride, copolymers of ethylene and of an unsaturated carboxylic acid anhydride, copolymers of ethylene and of an unsaturated epoxide, SBS- or SIS-type block copolymers grafted by a carboxylic acid or an unsaturated carboxylic acid anhydride as compatibilizer between a styrenic resin and a copolymer containing polyamide blocks and polyether blocks.

Other prior-art documents which may be cited are:

- EP 927727,
- *J. Polym. Sci.*, Part C: Polym. Lett. (1989), 27(12), 481
- *J. Polym. Sci.*, Part B, Polym. Phys. (1996), 34(7), 1289
- JAPS, (1995), 58(4), 753
- JP 04370156

- JP 04239045
- JP 02014232
- JP 11060855
- JP 11060856
- JP 09249780
- JP 08239530
- JP 08143780

The prior art demonstrates either blends (i) of styrenic resin and polyetheresteramide without compatibilizer or blends (ii) of polyetheresteramide and functionalized styrenic resin or else blends (iii) of polyetheresteramide, non-functionalized styrenic resin and functionalized styrenic resin.

The blends (i) are antistatic if the polyetheresteramide is carefully chosen, but have poor mechanical properties, elongation at failure in particular being much lower than that of the styrenic resin alone. As far as the blends (ii) and (iii) are concerned, it is necessary to have access to a functionalized styrenic resin, which is a complicated and costly matter. The object of the invention is to provide antistatic properties to the ordinary styrenic resins used to make the abovementioned articles, these being non-functionalized resins. It has now been found that when particular compatibilizers are used, one was able to obtain styrenic resin compositions which comprise a styrenic resin and a copolymer containing polyamide blocks and polyether blocks, and which have excellent elongation at failure, excellent tensile strength and excellent impact resistance (Charpy notched), when compared to the same composition without compatibilizer.

This invention provides a composition comprising per 100 parts by weight:

- From 99 to 60 parts by weight of a styrenic polymer (A),
- From 1 to 40 parts by weight of (B) + (C),

(B) being a copolymer containing polyamide blocks and polyether blocks comprising essentially ethylene oxide units $\text{---}(\text{C}_2\text{H}_4 \text{---}\text{O})\text{---}$, (C) being a compatibilizer chosen from block copolymers comprising at least one polymerized block comprising styrene and at least one polymerized block comprising methyl methacrylate, the weight ratio (B)/(C) being between 2 and 10.

As an example of a styrenic polymer (A), one may mention polystyrene, polystyrene modified by elastomers, random or block copolymers of styrene and dienes such as butadiene,

copolymers of styrene and of acrylonitrile (SAN), the SAN being modified by elastomers, in particular ABS, obtained, for example, by grafting (graft polymerization) of styrene and acrylonitrile on a base chain composed of polybutadiene or of butadiene-acrylonitrile copolymer, and blends of SAN and of ABS. The aforementioned elastomers may be, for example, EPR (abbreviation for ethylene propylene rubber or ethylene propylene elastomer), EPDM (abbreviation for ethylene propylene diene rubber or ethylene propylene diene elastomer), polybutadiene, acrylonitrile butadiene copolymers, polyisoprene, and isoprene acrylonitrile copolymers. In particular, A may be a high-impact polystyrene comprising a matrix of polystyrene surrounding rubber nodules generally comprising polybutadiene.

In the abovementioned polymers (A), part of the styrene may be replaced by unsaturated monomers copolymerizable with styrene, and as an example, one may mention alpha-methylstyrene and the (meth)acrylic esters. In this case, A may comprise a copolymer of styrene, among which one may mention styrene/alpha-methyl-styrene copolymers, styrene-chlorostyrene copolymers, styrene-propylene copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-vinyl chloride copolymers, styrene-vinyl acetate copolymers, styrene-alkyl acrylate copolymers (methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, phenyl acrylate), styrene-alkyl methacrylate copolymers (methyl methacrylate, ethyl methacrylate, butyl methacrylate, phenyl methacrylate), styrene-methyl chloroacrylate copolymers and styrene-acrylonitrile-alkyl acrylate copolymers. The content of comonomers in these copolymers is generally up to 20% by weight. This invention also provides high-melting-point metallocenic polystyrenes.

One would not exceed the scope of the invention, if (A) was a blend of two or more of the preceding polymers.

The styrenic polymer A preferably comprises more than 50% by weight of styrene. If the styrenic polymer is SAN, it preferably contains more than 75% by weight of styrene.

The polymers (B) containing polyamide blocks and polyether blocks are the result of copolycondensation of terminally reactive polyamide sequences with terminally reactive polyether sequences, including among others:

1) Polyamide sequences having diamine chain ends with polyoxyalkylene sequences having dicarboxylic chain ends.

2) Polyamide sequences having dicarboxylic chain ends with polyoxyalkylene sequences having diamine chain ends and obtained via cyanoethylation and hydrogenation of alpha-omega-dihydroxylated aliphatic polyoxyalkylene sequences known as polyetherdiols.

3) Polyamide sequences having dicarboxylic chain ends with polyetherdiols, the products obtained in this particular case being polyetheresteramides. The copolymers (B) are advantageously of this type.

The polyamide sequences having dicarboxylic chain ends derive, for example, from the condensation of alpha-omega-aminocarboxylic acids, lactams or dicarboxylic acids and diamines in the presence of a dicarboxylic acid as chain regulator.

The molecular mass expressed as \overline{M}_n of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5,000. The mass \overline{M}_n of the polyether sequences is between 100 and 6,000 and preferably between 200 and 3,000.

The polymers containing polyamide blocks and polyether blocks may also comprise randomly distributed units. These polymers may be prepared by means of the simultaneous reaction of the polyether and the precursors of the polyamide blocks.

For example, a reaction may be carried out using polyetherdiol, a lactam (or an alpha,omega-amino acid) and a diacid chain regulator in the presence of a little water. A polymer is obtained comprised essentially of polyether blocks, polyamide blocks of a highly variable length, and also various reactants, having reacted in a random manner, that are randomly distributed along the polymer chain.

These polymers containing polyamide blocks and polyether blocks, whether they derive from the copolycondensation of polyamide and polyether sequences prepared previously or from a one-step reaction, have for example Shore D hardnesses which can be between 20 and 75 and advantageously between 30 and 70, and an intrinsic viscosity between 0.8 and 2.5 measured in metacresol at 250° C for an initial concentration of 0.8 g/100 ml. The MFIs may be between 5 and 50 (235° C under a load of 1 kg).

The polyetherdiol blocks are either used as they stand and copolycondensed with the carboxylic-terminated polyamide blocks, or are aminated to be converted into polyetherdiamines and condensed with the carboxylic-terminated polyamide blocks. They may also be mixed with precursors of polyamide and a chain regulator to make polymers containing polyamide blocks and polyether blocks having randomly distributed units.

Polymers containing polyamide blocks and polyether blocks are described in the patents U.S. Pat. No. 4,331,786, U.S. Pat. No. 4,115,475, U.S. Pat. No. 4,195,015, U.S. Pat. No. 4,839,441, U.S. Pat. No. 4,864,014, U.S. Pat. No. 4,230,838 and U.S. Pat. No. 4,332,920.

In a first embodiment of the invention, the polyamide sequences having dicarboxylic chain ends derive, for example, from the condensation of alpha-omega-amino-carboxylic acids, lactams or dicarboxylic acids and diamines in the presence of a dicarboxylic acid chain regulator. By way of example of alpha-omega-amino-carboxylic acids, mention may be made of aminoundecanoic acid, and by way of example of a lactam mention may be made of caprolactam and lauryl lactam, and by way of example of dicarboxylic acid mention may be made of adipic acid, decanedioic acid and dodecanedioic acid, and by way of example of diamine mention may be made of hexamethylenediamine. The polyamide blocks are advantageously composed of polyamide-12 or polyamide-6. The melting point of these polyamide sequences, which is also that of the copolymer (B), is generally from 10 to 15° C below that of PA 12 or of PA 6.

Depending on the nature of (A), it can be useful to use a copolymer (B) whose melting point is lower in order to avoid degrading (A) during the incorporation of (B), and this is the subject of the second and third embodiments of the invention below.

In a second embodiment of the invention, the polyamide sequences are the result of condensation of one or more alpha-omega-aminocarboxylic acids and/or of one or more lactams having from 6 to 12 carbon atoms in the presence of a carboxylic diacid having from 4 to 12 carbon atoms, and are of low weight, i.e. \overline{M}_n from 400 to 1,000. As an example of alpha-omega-amino-carboxylic acid, one may mention aminoundecanoic acid and aminododecanoic acid. As an example of dicarboxylic acid, one may mention adipic acid, sebacic acid, isophthalic acid, butanedioic acid, 1,4-cyclohexyldicarboxylic acid, terephthalic acid, the sodium or lithium salt of sulfoisophthalic

acid, dimerized fatty acids (these dimerized fatty acids have a dimer content of at least 98% by weight and are preferably hydrogenated) and dodecanedioic acid $\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$.

By way of example of lactam, one may mention caprolactam and lauryl lactam.

Caprolactam should be avoided unless the polyamide is purified by removing the caprolactam monomer which remains dissolved within it.

Polyamide sequences obtained by means of condensation of lauryl lactam in the presence of adipic acid or of dodecanedioic acid and having a weight \overline{M}_n of 750 have a melting point of 127-130° C.

According to a third embodiment of the invention, the polyamide sequences result from the condensation of at least one alpha-omega-aminocarboxylic acid (or one lactam), at least one diamine and at least one carboxylic diacid. The alpha-omega-aminocarboxylic acid, the lactam and the carboxylic diacid may be chosen from those mentioned above.

The diamine may be an aliphatic diamine having from 6 to 12 atoms, or it may be an acrylic and/or saturated cyclic diamine.

By way of examples, one may mention hexamethylenediamine, piperazine, 1-aminoethylpiperazine, bisaminopropylpiperazine, tetramethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, 1,5-diaminohexane, 2,2,4-trimethyl-1,6-diaminohexane, diamine polyols, isophoronediamine (IPD), methylpentamethylenediamine (MPDM), bis(amino-cyclohexyl)methane (BACM), and bis(3-methyl-4-aminocyclohexyl)methane (BMACM).

In the second and third embodiments of the invention, the various components of the polyamide sequence and their ratios are chosen in order to obtain a melting point below 150° C and advantageously between 90 and 135° C. Low-melting-point copolyamides are described in the patents U.S. Pat. No. 4,483,975, DE 3 730 504, and U.S. Pat. No. 5,459,230. The same ratios of the components are utilized for the polyamide blocks of (B). (B) may also be the copolymers described in U.S. Pat. No. 5,489,667.

The polyether blocks may represent from 5 to 85% by weight of (B). The polyether blocks may contain units other than the ethylene oxide units, e.g. units of propylene oxide or of polytetrahydrofuran (which leads to polytetramethylene glycol chaining). One can also simultaneously use PEG blocks, i.e. blocks comprised of ethylene oxide units, PPG blocks, i.e.

blocks comprised of propylene oxide units, and PTMG blocks, i.e. blocks comprised of tetramethylene glycol units, also referred to as polytetrahydrofuran. Advantageously, one uses PEG blocks or blocks obtained by ethoxylation bisphenols, e.g. bisphenol A. These latter products are described in patent EP 613 919. The number of polyether blocks in (B) is advantageously from 10 to 50% by weight of (B) and preferably from 35 to 50%.

The copolymers of the invention may be prepared by any means permitting linkage of the polyamide blocks to the polyether blocks. Essentially, two processes are used in practice, one being a two-step process and the other being a single-step process.

The two-step process consists initially in preparing the carboxylic-terminated polyamide blocks via condensation of precursors of polyamide in the presence of a dicarboxylic acid chain regulator, and then, in a second step, of adding the polyether and a catalyst. If the precursors of polyamide are only lactams or alpha-omega-aminocarboxylic acids, a carboxylic diacid is added. If the precursors themselves comprise a carboxylic diacid, it is used in excess with respect to the stoichiometry of the diamines. The reaction usually takes place between 180 and 300° C, preferably from 200 to 260° C, with the pressure developing in the reactor being between 5 and 30 bar, and being maintained for about 2 hours. The pressure is slowly reduced to atmospheric pressure and then the excess water is distilled off, for example for one or two hours.

Once the carboxylic-terminated polyamide has been prepared, one adds the polyether and a catalyst. The polyether may be added in one or more portions, and the same applies to the catalyst. In one advantageous embodiment, the polyether is added first, and the reaction of the terminal OH groups of the polyether and the terminal COOH groups of the polyamide begins with formation of ester bonds and the elimination of water. One eliminates as much water as possible from the reactional medium by distillation, and then one introduces the catalyst in order to obtain the bond between the polyamide blocks and the polyether blocks. This second step is carried out while stirring, preferably under a vacuum of at least 5 mm of Hg (650 Pa) at a temperature such that the reactants and the copolymers obtained are molten. By way of example, this temperature may be between 100 and 400° C and more often between 200 and 300° C. The reaction is followed by measuring the torque exerted by the molten polymer on the stirrer or by measuring the electrical power consumed by the stirrer. The end of the reaction is determined by the torque value or target power value.

The catalyst is defined as being any material making it easier to bond the polyamide blocks to the polyether blocks via esterification. The catalyst is advantageously a derivative of a metal (M) chosen from the group formed by titanium, zirconium and hafnium.

As an example of a derivative, one may mention the tetraalkoxides complying with the general formula $M(OR)_4$, in which M represents titanium, zirconium or hafnium and the Rs, identical or different, indicate linear or branched alkyl radicals having from 1 to 24 carbon atoms.

Examples of the C_1 to C_{24} -alkyl radicals among which the radicals R are chosen for the tetraalkoxides used as catalysts in the process according to the invention are methyl, ethyl, propyl, isopropyl, butyl, ethylhexyl, decyl, dodecyl, and hexadecyl. The preferred catalysts are the tetraalkoxides for which the radicals R, identical or different, are the C_1 - C_8 -alkyl radicals. Particular examples of these catalysts are $Zr(OC_2H_5)_4$, $Zr(O\text{-}isoC_3H_7)_4$, $Zr(OC_4H_9)_4$, $Zr(OC_5H_{11})_4$, $Zr(OC_6H_{13})_4$, $Hf(OC_2H_5)_4$, $Hf(OC_4H_9)_4$, $Hf(O\text{-}isoC_3H_7)_4$.

The catalyst used in this process according to the invention may consist solely of one or more tetraalkoxides defined above having the formula $M(OR)_4$. It may also be formed by combining one or more of these tetraalkoxides with one or more alkaline or alkaline-earth alcoholates having the formula $(R_1O)_pY$ in which R_1 indicates a hydrocarbon residue, advantageously a C_1 to C_{24} -alkyl residue, and preferably C_1 to C_8 , Y represents an alkali metal or alkaline earth metal, and p is the valency of Y. The amounts of alkaline or alkaline earth alcoholate, and zirconium or hafnium tetraalkoxides that one combines to constitute the mixed catalyst may vary within wide limits. However, it is preferable to use alcoholate and tetraalkoxides quantities such that the molar proportion of alcoholate is approximately equal to the molar proportion of tetraalkoxide.

The proportion by weight of catalyst, i.e. of the tetraalkoxide(s) if the catalyst does not include alkali or alkaline earth alcoholate, or else of the entirety of the tetraalkoxide(s) and of alkali or alkaline earth alcoholate(s) if the catalyst is formed by combining these two types of compound, advantageously varies from 0.01 to 5% by weight of the mixture of the dicarboxylic polyamide with the polyoxyalkylene glycol, and is preferably between 0.05 and 2% of that weight.

As examples of other derivatives, one may mention the salts of the metal (M), in particular the salts of (M) and an organic acid, and the complex salts of the oxide of (M) and/or the hydroxide of (M) and an organic acid. The organic acid may advantageously be formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, salicylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, phthalic acid and crotonic acid. Acetic and propionic acids are particularly preferred. M is advantageously zirconium. These salts may be termed zirconyl salts. Without being bound by this explanation, the Applicant thinks that these salts of zirconium with an organic acid or the complex salts mentioned above release ZrO^{++} during the course of the process. One uses the product sold under the name of zirconyl acetate. The amount to use is the same as that for the M(OR)_4 derivatives.

This process and these catalysts are described in the patents U.S. Pat. No. 4,332,920, U.S. Pat. No. 4,230,838, U.S. Pat. No. 4,331,786, U.S. Pat. No. 4,252,920, JP 07145368A, JP 06287547A and EP 613919.

With respect to the single-step process, one mixes all the reactants used in the two-step process, i.e. the precursors of polyamide, the carboxylic diacid chain regulator, the polyether and the catalyst. The reactants and the catalyst are the same as those in the two-step process described above. If the precursors of polyamide are only lactams, it is advantageous to add a little water.

The copolymer essentially has the same polyether blocks and the same polyamide blocks, but also has a small fraction of the various reactants, which have reacted in a random manner, randomly distributed along the polymer chain.

The reactor is closed and heated, with stirring, as in the first step of the two-step process described above. The pressure that develops is between 5 and 30 bar. Once the pressure stops climbing, one places the reactor under reduced pressure while maintaining vigorous stirring of the molten reactants. The reaction is followed as above for the two-step process.

The catalyst used in this one-step process is preferably a salt of the metal (M) and an organic acid, or a complex salt of the oxide of (M) and/or the hydroxide of (M) and an organic acid.

The ingredient (B) may also be a polyetheresteramide (B) having polyamide blocks comprising sulfonates of dicarboxylic acids either as chain regulators for the polyamide block or in association with a diamine as one of the monomers constituting the polyamide block, and having polyether blocks essentially consisting of alkylene oxide units, as described in the international application PCT/FR00/02889.

The compatibilizer C is a block copolymer comprising at least one polymerized block comprising styrene and at least one polymerized block comprising methyl methacrylate.

The polymerized block comprising styrene is generally present in C in a proportion of from 20 to 80% by weight.

The polymerized block comprising methyl methacrylate is generally present in C in a proportion of 20 to 80% by weight.

The polymerized block comprising styrene generally has a glass transition temperature above 100° C and preferably comprises at least 50% by weight of styrene. The polymerized block comprising styrene may also comprise an unsaturated epoxide (obtained by copolymerization), this latter preferably being glycidyl methacrylate. The unsaturated epoxide may be present in a proportion from 0.01% to 5% by weight in the polymerized block comprising styrene.

The polymerized block comprising methyl methacrylate generally has a glass transition temperature above 100° C and preferably comprises more than 50% by weight of methyl methacrylate. The polymerized block comprising methyl methacrylate may also comprise an unsaturated epoxide (obtained by copolymerization), this latter preferably being glycidyl methacrylate. The unsaturated epoxy may be present in a proportion from 0.01% to 5% by weight in the polymerized block comprising methyl methacrylate.

The copolymer having blocks comprising at least one polymerized block comprising styrene and at least one polymerized block comprising methyl methacrylate may also be grafted by an unsaturated epoxide, preferably glycidyl methacrylate.

As an example of unsaturated epoxides, one may mention:

- The aliphatic glycidyl esters and aliphatic glycidyl ethers, such as allyl glycidyl ether, vinyl glycidyl ether, glycidyl maleate and glycidyl itaconate, glycidyl(meth)acrylate, and

- The alicyclic glycidyl esters and alicyclic glycidyl ethers, such as 2-cyclohexene-1- glycidyl ether, diglycidyl cyclohexene-4,5-dicarboxylate, glycidyl cyclohexene-4-carboxylate, glycidyl 2-methyl-5-norbornene-2-carboxylate and diglycidyl cis-endo-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylate.

In the block comprising styrene, part of the styrene may be replaced by unsaturated monomers copolymerizable with styrene, and as an example, one may mention alpha-methylstyrene and the (meth)acrylic esters. In this case, the block comprising styrene is a copolymer of styrene, examples of which one can mention as being styrene-alpha-methylstyrene copolymers, styrene-chlorostyrene copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-vinyl chloride copolymers, styrene-vinyl acetate copolymers, styrene-alkyl acrylate copolymers (methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, phenyl acrylate), styrene-alkyl methacrylate copolymers (methyl methacrylate, ethyl methacrylate, butyl methacrylate, phenyl methacrylate), styrene-methyl chloroacrylate copolymers and styrene-acrylonitrile-alkyl acrylate copolymers.

In particular, C may be:

- A diblock copolymer comprising a block of a polymer of styrene and a block of a polymer of methyl methacrylate;
- A diblock copolymer comprising a block of a polymer of styrene and a block of poly(methyl methacrylate-co glycidyl methacrylate);
- A diblock copolymer of a polymer of styrene-polymer of methyl methacrylate, said copolymer being grafted by glycidyl methacrylate;
- A diblock copolymer comprising a block of homopolystyrene and a block of methyl homopolymethacrylate;
- A diblock copolymer comprising a block of homopolystyrene and a block of poly(methyl methacrylate-co glycidyl methacrylate);
- A diblock copolymer of homopolystyrene-methyl homopolymethacrylate, said copolymer being grafted by glycidyl methacrylate;
- A diblock copolymer comprising a block of polystyrene-co-glycidyl methacrylate and a block of methyl polymethacrylate;

- A diblock copolymer comprising a block of polystyrene-co-glycidyl methacrylate and a block of poly(methyl methacrylate-co-glycidyl methacrylate).

In addition, C may also be a triblock copolymer S-B-M, S representing the polymerized block comprising styrene, M representing the polymerized block comprising methyl methacrylate, and B representing an elastomeric block having a glass transition temperature (T_g) below 5°C , preferably below 0°C , and most preferably below -40°C .

The monomer used to synthesize elastomeric block B may be a diene selected from butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 2-phenyl-1,3-butadiene. B is advantageously selected from the poly(dienes), especially poly(butadiene), poly(isoprene), and their random copolymers, or also among the partially or completely hydrogenated poly(dienes). Among the polybutadienes, one advantageously uses those whose T_g is lowest, for example 1,4-polybutadiene having a T_g (around -90°C) below that of 1,2-polybutadiene (around 0°C). The B blocks may also be hydrogenated. One performs this hydrogenation according to usual methods.

The monomer used to synthesize elastomeric block B may also be an alkyl (meth)acrylate. One then obtains the following T_g in parentheses following the name of the acrylate: ethyl acrylate (-24°C), butyl acrylate (-54°C), 2-ethylhexyl acrylate (-85°C), hydroxyethyl acrylate (-15°C), and 2-ethylhexyl methacrylate (-10°C). One advantageously uses butyl acrylate.

Preferably, blocks B are constituted for the most part of 1,4-polybutadiene.

Thus, C may be:

- A triblock copolymer S-B-M in which S is a block of a styrene polymer, B is a block of polybutadiene, and M is a block of a methyl methacrylate polymer.

- A triblock copolymer S-B-M in which S is a block of homopolystyrene, B is a block of polybutadiene, and M is a block of methyl homopolymethacrylate.

One would not exceed the scope of the invention by utilizing one or multiple compatibilizers C.

The compatibilizer C may in particular be prepared by controlled free-radical polymerization methods in the presence of a stable free radical (generally a nitroxide) according to the principle taught in EP 927727. The SBMs may be obtained by anionic synthesis.

The level of antistatic properties increases with the proportion of (B) and, for equal amounts of (B), with the proportion of ethylene oxide units present in (B).

According to the application, preference will be given to including a proportion of (B) sufficient to obtain, in the final composition, a surface resistivity measured according to the standard IEC93 below $5 \cdot 10^{13}$ O/□. According to the application, preference will be given to including a proportion of (B) sufficient to give the final composition a volume resistivity measured according to standard IEC93 below $5 \cdot 10^{16}$ O.cm.

The amount of (B) + (C) is advantageously from 5 to 30 parts per 95 to 70 parts of (A) and preferably from 10 to 20 per 90 to 80 parts of (A). The (B)/(C) ratio is advantageously between 4 and 10. The amount of C in the composition may be from 0.5 to 5 parts by weight per 100 parts by weight of composition.

One would not exceed the scope of the invention by adding mineral fillers (talc, Ca_3CO_3 , kaolin, etc.), reinforcing agents (glass fiber, mineral fiber, carbon fiber, etc.), stabilizers (heat, UV), flame retardants and colorants.

The compositions of the invention are prepared by the methods usual for thermoplastics, e.g. by extrusion or with the aid of twin-screw mixers.

This invention also relates to articles manufactured with the preceding compositions; examples of these are films, pipes, sheets, packaging, as well as cases for computers, fax machines or telephones.

In the examples hereafter, the following abbreviations are used:

- GMA: glycidyl methacrylate;
- MAM: methyl methacrylate;
- SM: polystyrene block of methyl polymethacrylate;
- SM/GMA: polystyrene block of methyl polymethacrylate grafted/copolymerized by glycidyl methacrylate;
- PEG: polyethylene glycol;
- PMMA: poly(methyl methacrylate);

- Mw: weight average molecular weight;
- Mn: number average molecular weight;
- Mw/Mn: polydispersity;
- Rv: volume resistivity (Ω.cm);
- Rs: surface resistivity (Ω/□);
- HO-TEMPO: 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy usually sold under the name of 4-hydroxy TEMPO;

- SEC: steric exclusion chromatography;
- LAC: liquid adsorption chromatography;
- GPC: gel permeation chromatography;
- RMN: nuclear magnetic resonance;
- TEM: transmission electron microscopy;

In the examples that follow, the ingredients below are used:

- PS 4241: styrene-butadiene copolymer. This copolymer has a fluidity index between 3 and 5 g/10 min (ISO 1133.91) at 200°C under 5 kg. It is also characterized by a Vicat temperature of 97°C (ISO 306A50). This copolymer has a styrene content of about 95% by weight. This copolymer is sold by the company ATOFINA under the brand name of Lacqrene.

- MH1657: copolyether-block-amide having blocks of polyamide 6 of a number average molecular weight of 1,500 and PEG blocks of a number average molecular weight of 1,500; the melting point is 204°C. This copolymer is sold by the company ATOFINA under the brand name of Pebax MS1657.

- SM: this is a copolymer having a polystyrene block-(methyl polymethacrylate) block prepared by controlled free-radical polymerization with an Mw = 106,000 and a polydispersity of 2.1. The styrene content is 61% by weight.

- SM/GMA: this is a copolymer having a polystyrene block-methyl methacrylate-co-glycidyl methacrylate block prepared by a controlled free-radical polymerization having an Mw = 108,700 and a polydispersity of 2.0. The styrene content is 65% by weight and it contains 0.4% GMA by weight.

In the examples that follow, the characterization methods listed below were used:

- Mechanical properties:

The compositions obtained are injected under pressure at temperatures between 220 and 240°C in the form of dumbbell-shaped pieces, bars, or sheets. The dumbbell-shaped pieces allow one to perform ISO R527 tension tests and the bars are used for the notched Charpy impact test according to ISO 179:93 1eA.

- Antistatic properties:

Sheets sized 100x100x2 mm³ are injected molded and allow one to perform resistivity measurement tests according to standard IEC-93.

In the tables, the measured volume resistivity is given in ohm.cm, while the measured surface resistivity is given in ohm/□. The properties obtained under tension are also given.

All tests are performed at 23°C. The sheets are conditioned at 50% humidity for 15 days prior to being tested for the surface resistivity measurement.

Examples 1 to 6

a) Preparation of compatibilizers C (description of the synthesis procedure for SM and SM/GMA)

One uses two steel, dual-jacket reactors in series. The reactors are connected by insulated piping and wrapped in heater cable to prevent any cooling during casting.

The styrene, the solvent, the catalyst and the OH-TEMPO (belonging to the nitroxide family) are introduced into the reactor under atmospheric pressure, then heated to 140°C. A kinetic test is performed on the reactive mixture and that is why samples are taken when the reaction mixture's temperature reaches about 130°C. All these samples are flashed (at 170°C under vacuum in a bell jar) in order to determine the conversion rate of styrene and polystyrene. After about a 60-70% conversion into polystyrene, one adds all at once the methyl methacrylate previously heated in the aforementioned reactor to 100°C.

The reaction mixture is brought to about 140°C during approximately 3 hours and then subjected to devolatilization so as to eliminate the volatile compounds. The copolymer is recovered in the form of granules.

The following table shows the quantities of reactants used in the first stage of synthesis for these two tests.

Ingredients used	Synthesis of a polystyrene-b-PMMA (SM)	Synthesis of a polystyrene-b-(PMMAgGMA) (SM/GMA)
Styrene in g	2,850	2,850
Ethylbenzene in g	500	500
HO-TEMPO in g	3.51	3.51
Dicumyl peroxide in g	5.61	5.61
Methyl methacrylate in g	6,650	6,555
Glycidyl methacrylate in g	0	95
Polymerization time of styrene in min.	120	150
Copolymerization time in min.	150	150

Experimental conditions:

Temperature of oil bath: 160°C, temperature of condenser: -20°C. The start time to convert the styrene is selected when the temperature of the polymerization medium reaches 130°C.

The quantity of MAM (or MAM/GMA mixture) is pre-heated to the boiling point before being added to the reaction mixture. The temperature of the oil bath is left constant at 160°C. The condenser valve is in the closed position. The temperature stabilizes as the pressure in the reactor increases ($P=1.5$ bar) at 120°C. The product is then recovered in the form of granules. The product is analyzed by means of LAC, GPC, and RMN as well as TEM after having made a film by slow evaporation in chloroform.

In addition to these SEC analyses, quantitative LAC analyses were performed. With this method, it was possible to quantify the content of homopolystyrene and homoPMMA present in the reaction mixture, then to determine the composition by mass of polystyrene and PMMA of the copolymers. Lastly, a RMN analysis of the reaction mixture also allowed us to determine the contents of the MMM, SMS, and MMS triad representing the copolymer in block or random form (MMM=three units of neighboring MAM, SMS = unit of styrene followed by MAM which is followed by S, and MMS = unit of MAM followed by MAM which is followed by styrene). Determining this content allows one to characterize the structuring of

the block copolymer. A percentage of 100% of the MMM triad signifies a perfect structuring.

All results are depicted in the following table:

	SM	SM/GMA
Mw (g/mole)	106,000	108,700
Mw/Mn	2.1	2
%PS gross (by weight)	61	65
%GMA	0	0.4
% homopolystyrene by weight	29	30
% copolymer by weight	71	70
Average composition of PS/PMMA copolymer	45/55	
% MMM triad	74	

All of these results show that the products obtained are rich in block copolymers since once the homopolystyrene content is near 30%, there is no PMMA homopolymer and lastly the MMM triad content is greater than 70%. Also, the TEM analyses of these products show lamellar structures. Regardless of the test, the structure obtained is always the lamellar type throughout the entire space. One can observe that the polystyrene platelets are inflated by the homopolystyrene since the thicknesses of these platelets are greater than those of the PMMA even though the composition of the copolymer is on the order of 50/50.

The copolymer having a polystyrene block-PMMA block has a styrene content of 45% by weight and a MAM content of 55% by weight.

b) Preparing the compositions by extruder mixing

One uses a double-screw extruder made by Werner and Pfleiderer having a 30-mm diameter with a total output of 20 kg/hr. This output represents the sum of the outputs of the ingredients used. The temperature settings for the ducts range from 230 to 250°C. The extruded strings coming out of the machine are cooled in a water trough and are transformed into granules. These granules are injected in the form of plates, rods, or dumbbell-shaped pieces at similar temperatures (230 to 250°C).

The results recorded in the table above highlight the compatibilizing action of the copolymers having SM and SM/GMA blocks. The block copolymers were used as obtained without separation in relation to the homopolystyrene that was mixed in with it. This homopolystyrene may

be considered as being a styrenic resin (A). In the results table below, the quantities of SM and SM/GMA indicated correspond to quantities of pure copolymers. The quantities of homopolystyrene added at the time of adding the block copolymer are recorded in the second line of the table.

Example #	1	2	3	4	5	6
PS 4241	100	90	88	88	86	86
Homopolystyrene			0.6	0.6	1.2	1.2
MH 1657		10	10	10	10	10
Polystyrene-b-PMMA			1.4		2.8	
Polystyrene-b-(PMMAgGMA)				1.4		2.8
Rv (O.cm)	1.40E+17	8.20E+13	2.50E+15	2.60E+15	2.50E+16	2.60E+15
Rs (O/□)	2.30E+15	1.10E+12	3.70E+12	3.00E+12	1.10E+13	3.90E+12
Charpy notched ISO 179:93 1eA						
+23°C kJ/m ²	11.1	7.1	8.6	11.1	10.9	11.1
Tension fatigue failure 23°C ISO 527:93-1B, v=50 mm/min						
Sigma threshold (Mpa)	27.4	24.4	25	25.5	25.8	26
% threshold	1.4	1.5	1.4	1.5	1.5	1.5
Sigma failure (Mpa)%	22.7	17	19.4	21.9	22.1	22.4
% failure	56.3	24.2	36.5	54.6	55.5	59

In fact, the elongation at failure and the strain at failure are improved while the matrix's impact properties are maintained and the composition is made antistatic.

The influence of block copolymers is also visible from the perspective of the particles' size. In test 1, the size of the particles is on the order of 1µm, while for examples 5 and 6 it is reduced by half (0.5 µm). The size reduction of the particles is generally accompanied by improved compatibilizing action of the block copolymer.

Claims

1. A composition comprising, per 100 parts by weight:
 - From 99 to 60 parts by weight of a styrenic polymer (A),
 - From 1 to 40 parts by weight of (B) + (C),(B) being a copolymer containing polyamide blocks and polyether blocks essentially comprising ethylene oxide units $-(C_2H_4 - O)-$, and (C) being a compatibilizer selected from block copolymers comprising at least one polymerized block comprising styrene and at least one polymerized block comprising methyl methacrylate units, the (B)/(C) ratio by weight being between 2 and 10.
2. Composition according to claim 1 wherein the proportion of (B) is sufficient to give the final composition a surface resistivity measured according to standard IEC93 is below $5 \cdot 10^{13} \text{ O}/\square$.
3. Composition according to one of the previous claims wherein the proportion of (B) is sufficient to give the final composition a volume resistivity measured according to standard IEC93 below $5 \cdot 10^{16} \text{ O} \cdot \text{cm}$.
4. Composition according to one of the previous claims, wherein (A) comprises more than 50% styrene.
5. Composition according to one of the previous claims, characterized in that the quantity (C) ranges from 0.5 to 5 parts by weight in 100 parts by weight of said composition.
6. Composition according to one of the previous claims, characterized in that the polymerized block comprising styrene is present in C in a proportion of 20 to 80% by weight.
7. Composition according to one of the previous claims, characterized in that the polymerized block comprising methyl methacrylate is present in C in a proportion of 20 to 80% by weight.
8. Composition according to one of the previous claims, characterized in that the polymerized block comprising styrene comprises at least 50% styrene by weight.
9. The polymerized block comprising styrene comprises glycidyl methacrylate.
10. Composition according to one of the previous claims, characterized in that the polymerized block comprising methyl methacrylate comprises more than 50% methyl methacrylate by weight.

11. Composition according to one of the previous claims, characterized in that the polymerized block comprising methyl methacrylate comprises glycidyl methacrylate.

12. Composition according to one of the previous claims, characterized in that the block copolymer comprising at least one polymerized block comprising styrene and at least one polymerized block comprising methyl methacrylate is grafted by glycidyl methacrylate.

13. Composition according to one of the previous claims, characterized in that (A) is a styrene-butadiene copolymer.

14. Composition according to one of the previous claims, wherein the quantity (B) + (C) is 5 to 30 parts for every 95 to 70 parts of (A).

15. Composition according to one of the previous claims, wherein the quantity (B) + (C) is 10 to 20 parts for every 90 to 80 parts of (A).

16. Composition according to one of the previous claims, characterized in that (C) is a triblock copolymer S-B-M, S representing the polymerized block comprising styrene, M representing the polymerized block comprising methyl methacrylate, and B representing an elastomeric block having a glass transition temperature (T_g) below 5°C.

17. Objects manufactured having a composition according to one of the previous claims.

18. Utilization of the object of the preceding claim to come into contact with electronic components.

Republic of France

INPINational Institute of
Industrial Property**Preliminary Research
Report**Based upon the most recent
claims filed prior to initiating
research

National Registration No.

FA 598725
FR 0101214

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim no.	Classification assigned to invention by INPI
Category	Citation of document with indication where appropriate of the relevant passages		
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Category of cited documents X: Particularly relevant on its own. Y: Particularly relevant combined with another document of the same category. A: Technological background O: Oral disclosure P: Document published after priority date and prior to filing date. T: Theory or principle upon which invention is based. E: Patent document dated prior to the filing date and published on or after that date. D: Cited in the application. L: Cited for other reasons. &: Member of same family, corresponding document.			

Annex to the Preliminary Research Report
Pertaining to the French Patent Application No. FR 0101214 FA 598725

This annex indicates the members of the patent families relating to the patent documents cited in the aforementioned preliminary research report.

Said members are stored on a computer file at the European Patent Office as of October 1, 2001.

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For any information regarding this annex, please see the *Official Journal* of the European Patent Office, No. 12/82.